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(54) Process for the elimination of  
mercaptans contained in gas

(57) Mercaptans contained in various  
gases, and especially in natural gases  
are absorbed in a hydrocarbon oil and  
the oil regenerated by oxidation to  
sulfonic acids of the mercaptans  
contained therein.

The oxidation is carried out at  
absorption temperature and pressure  
by means of an oxidant such as  
hydrogen peroxide or a peracid in an  
aqueous medium. The regenerated oil  
is recycled after separation from the  
aqueous phase containing the sulfonic  
acids in solution.

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## SPECIFICATION

Process for the elimination of mercaptans contained in gas

## Background of the invention

## 5 Field of the invention

The present invention concerns a process for the elimination of the mercaptans contained in different gas compositions and especially in natural gas.

- 10 The sulfur containing gases in general contain sulfur in the form of hydrogen sulfide contaminated by a variable quantity of mercaptans. These gases are treated in desulfuration units that operate either with
- 15 "physical solvents" or with "chemical solvents". The "physical solvents", such as used in the SELEXOL, RECTISOL, PURISOL, SULFINOL processes absorb hydrogen sulfide and mercaptans; the desulfuration is complete. On the
- 20 other hand, in units that operate with "chemical solvents" such as monoethanolamine, diethanolamine or methyldiethanolamine salts are only formed with the acid components of the gas, i.e. the hydrogen sulfide and the carbon dioxide,
- 25 while the mercaptans essentially remain in the treated gas.

- If this gas containing the mercaptans also contains higher hydrocarbons of which the recovery is economically justified it is subjected to
- 30 an oil stripping treatment. This treatment consists, for example, in washing the gas with an oil at very low temperature (lower or equal to  $-30^{\circ}\text{C}$ ). This oil simultaneously absorbs the mercaptans, said mercaptans, after the fractioned
- 35 desorption resulting from the expansion being found in the hydrocarbon fraction having the corresponding boiling point.

- In the gas of commercial value, the total quantity of sulfur must be lower than  $50\text{ mg/m}^3$ , and for the gases to be used in reforming units the specifications are even more strict. Thus, for the majority of the sulfur containing gases treated in desulfuration units making use of "chemical
- 40 solvents" (amines) and which are not subsequently submitted to an oil stripping treatment, a supplementary purification is necessary.

## Summary of the prior art

- A process to be used for this supplementary
- 50 purification is the UOP so called MEROX process. In this process the gas to be purified is countercurrently washed by an aqueous soda solution containing the MEROX catalyst. The extracted mercaptans are oxidized by the oxygen
- 55 contained in the air to form disulfides. These latter are insoluble in the aqueous soda solution and are separated by decantation.

- The extraction of the methyl mercaptan by the aqueous soda solution is easy; it is however more
- 60 and more difficult for the upper homologs.

On the other hand, due to the common presence of carbon dioxide in the gas to be

treated there is irreversible consumption of the soda.

## 65 Summary of the invention

The present invention allows to overcome these drawbacks and especially to eliminate all the types of mercaptans contained in the treated gases.

- 70 This invention concerns a process for the elimination of the mercaptans contained in gases by absorption in a hydrocarbon oil and regeneration of this oil whereby said oil is regenerated by oxidizing the mercaptans it contains to form sulfonic acids, said oxidation
- 75 being carried out at the temperature and pressure of absorption by means of an oxidant, in aqueous medium, the regenerated oil being recycled after separation of the aqueous phase containing the sulfonic acids in solution.

- The gases containing mercaptans are countercurrently treated in an absorption column by a hydrocarbon oil. This column is operated at the pressure of the gas to be treated, in general
- 85 between 5 and 10 MPa, the temperature varying between ambient temperature and  $60^{\circ}\text{C}$ .

- Under these conditions, the oil absorbs, on the one hand, the mercaptans, and on the other hand, a certain quantity of the hydrocarbons contained
- 90 in the gas, this quantity being a Henry's Law function of the partial pressure of each of the hydrocarbons.

- In classic gasoline recovery, the regeneration of the oil and the recovery of the hydrocarbons is carried out by fractional expansion, the mercaptans being present in the hydrocarbon
- 95 fraction of corresponding boiling point; for example, methylmercaptan is present in the propane fraction.

- The particular proposed regeneration according to the invention allows the selective elimination of the mercaptans. This regeneration takes place at the same temperature and at the same pressure as the absorption. Due to this fact,
- 105 the recycled oil remains permanently charged with hydrocarbons in the proportions that correspond to the gas-liquid equilibrium at the temperature and pressure conditions of the absorber.

- The regeneration is carried out by a chemical
- 110 process consisting in the oxidation of the mercaptans in sulfonic acids. These latter are soluble in the aqueous phase that contains the oxidant and are insoluble in the oil.

- The oxidation is carried out in a reactor in which are simultaneously injected and preferably countercurrently, the mercaptan containing oil to be regenerated and the oxidant in aqueous
- 115 medium. This reactor must ensure a good contact between the two phases. In particular, a plate or packed column is used, for example, a Raschig rings column, ensuring a good liquid-liquid
- 120 contact. It is also possible to use a bubble column.

- The reaction medium withdrawn from the regeneration column is sent into a decanter.

- 125 The hydrocarbon loaded oily phase, from which the mercaptans have been eliminated, is recycled

towards the absorber. The aqueous phase containing the sulfonic acids is eliminated; however, where the oxidation agents have been used in an excess with respect of the mercaptans, the non-utilized quantities are present in this aqueous phase that is thus advantageous to recycle after, on the one hand, addition conversion after a certain time. This time is that much shorter (the reaction speeds thus much higher) when:

- the  $H_2O_2/RSH$  ratio is higher
- the quantity of organic acid present is higher
- the temperature is higher
- the contact between the two phases is improved.

Given that with the use of excess quantities of hydrogen peroxide these excess quantities do not decompose but are present in the aqueous effluents of the reactor, also to be recycled, there would be no hesitation in using excess hydrogen peroxide even 100 moles per mole of mercaptan, in order to profit from the high reaction speeds.

The recycling of aqueous effluents, after addition of make up hydrogen peroxide, also allows to considerably reduce the organic acid consumption.

Indeed, this acid in its peracid form acts as an active oxygen vector, but is integrally recovered at the end of the process. It is thus sufficient to add, during continuous operation, quantities of organic acid corresponding to those eliminated in a small purge flow of the aqueous phase loaded with sulfonic acids (these sulfonic acids furthermore facilitate the oxidation of the mercaptans by contributing to catalyse this reaction).

The oil used for the absorption of the mercaptans must be easily available, sufficiently fluid at operating temperature and hardly volatile at this temperature in order to minimize the losses through of make up oxydation agent, on the other hand, a given discharge.

The whole of these operations can be conducted either continuously or discontinuously (in batch).

Any hydrosoluble oxidant able to oxidize the mercaptans and form sulfonic acids is suitable to carry out the process according to the invention; particularly appropriate are hydrogen peroxide, or peracids such as performic or peracetic acid.

According to a preferred process for carrying out the invention, the oxidation agent is constituted by a peracid formed in situ from the reaction between a carboxylic acid and hydrogen peroxide.

Any concentration of hydrogen peroxide is suitable. For the sake of security, operation is limited to the use of solutions of 50% volume. Solutions of about 30% volume hydrogen peroxide are preferred.

The carboxylic acid used has the general formula  $R-COOH$ . R is an alkyl, halogeno-alkyl or aryl radical.

Easily water-soluble acids are preferred, such as those for which  $R=H, CH_3, CF_3$ . Formic acid leads to the highest reaction speeds. This acid is used at a ratio of 0.1 to 1 moles per mole of hydrogen peroxide, preferably 0.2 to 0.5 mole per mole  $H_2O_2$ .

Experience shows that the consumption of hydrogen peroxide is comprised approximately between 3 and about 12 moles per mole of mercaptan. Provided the hydrogen peroxide is present in a sufficient excess, the oxidation reaction of the mercaptans will reach total vapor pressure.

Oils such as spindle oil, 100 NS oil or any other refining cut with equivalent properties is preferably used.

It is not possible to generalize the composition of the oil that circulates in the system since it is permanently loaded with hydrocarbons that issue from the gas to be treated, in proportions that correspond to the gas-liquid equilibrium between this oil and the gas under temperature and pressure conditions at which the absorber operates. The composition of the oil is thus a function of the composition of the treated gas.

As indicated herein-above, the absorption and regeneration steps according to the present invention are carried out at the same pressure and at the same temperature, this pressure varying between 5 and 10 MPa and this temperature varying between 15 and 60°C.

#### 95 Example

2 000 000  $S/m^3/d$  of a natural gas having the composition indicated herein-under is treated in a conventional desulfuration unit making use of diethanolamine, under a pressure of 7 MPa:

	% Volumes
$N_2$	1.4
$CH_4$	71.1
$C_2H_6$	2.5
$C_3^+$	traces
$H_2S$	15.1
$CO_2$	9.9
$COS$	0.05
RSH	780 $mg/m^3$ expressed in sulfur

At the exit of this primary desulfuration installation the flow-rate is of 1.500 000  $Sm^3/d$  gas at 50°C and under 7 MPa, which gas presents the following compositions:

	ppm volumes
$CO_2$	1200
$H_2S$	4
$CH_3SH$	216
$C_2H_5SH$	75
$C_3H_7SH$	33
$C_4H_9SH$	17

This gas is thereafter countercurrently washed by a flow-rate of 140  $m^3/h$  spindle oil, having a specific gravity of 0.908, in an absorber

comprising 24 perforated plates operating at 50°C under 7 MPa.

The purified gas obtained at the head of this absorber presents the following composition;

5		<i>ppm volumes</i>
	CO <sub>2</sub>	1200
	H <sub>2</sub> S	3
	CH <sub>3</sub> SH	20
	C <sub>2</sub> H <sub>5</sub> SH	5
10	C <sub>3</sub> H <sub>7</sub> SH	2
	C <sub>4</sub> H <sub>9</sub> SH	1

The residual mercaptans correspond to the presence of 38 mg of sulfur/Sm<sup>3</sup>. The yield of the mercaptans elimination is 92%

15 The oil loaded with mercaptans, drawn from the bottom of the absorber contains:

	<i>mercaptans</i>	<i>ppm weight</i>
	CH <sub>3</sub> SH	195
	C <sub>2</sub> H <sub>5</sub> SH	90
20	C <sub>3</sub> H <sub>7</sub> SH	49
	C <sub>4</sub> H <sub>9</sub> SH	30

This loaded oil is thus injected at the bottom of a column packed with Raschig rings; it is therein counter-currently treated by 6.8 m<sup>3</sup>/h of an aqueous solution containing 8.74 K moles of hydrogen peroxide and 3.97 K moles of formic acid per m<sup>3</sup>. This regeneration column operates at the same pressure as the absorption column thus at 7 MPa. It is maintained at 50°C by immersed cooling circuits.

30 This aqueous solution was initially constituted by simultaneous injection in the storage tank of the aqueous solution of 30% volume hydrogen peroxide and pure formic acid, in the volume ratio 6/1.

35 The organic phase constitutes the continuous phase of the packed column. The working volume of the reactor allows to ensure a reaction time of 0.4 hours. After drawing off the regenerated oil at the head of the reactor, an analysis of the mercaptans it contains reveals the presence of the following constituents in the mentioned proportions:

	<i>mercaptan</i>	<i>ppm weight</i>
45	CH <sub>3</sub> SH	10
	C <sub>2</sub> H <sub>5</sub> SH	6
	C <sub>3</sub> H <sub>7</sub> SH	8
	C <sub>4</sub> H <sub>9</sub> SH	6

50 This analysis reveals an average elimination of 93% of the mercaptans initially present in the loaded oil. After transit in a storage tank, this oil is reinjected at the head of the washing column of the gas to allow the further absorption of the mercaptans.

55 The aqueous phase drawn off at the bottom of the oil regeneration column is directed towards a storage tank.

The analysis of this aqueous solution shows

that its formic acid content has not changed; it contains, furthermore, sulfonic acids corresponding to the transformed mercaptans; it still contains 8.23 K moles of hydrogen peroxide per m<sup>3</sup>.

60 The hydrogen peroxide consumption is established at 4.5 moles per mole of transformed mercaptan.

65 The titre adjustment of this aqueous solution is achieved through the addition of 361 litres/h 50% volume hydrogen peroxide to 6.44 m<sup>3</sup>/h of aqueous solution drawn off the storage tank.

70 Furthermore, an equivalent flow rate of purge (361 l/h) is drawn off the storage tank.

To compensate the loss of formic acid it is necessary to add 54 l/h fresh make-up acid.

## 75 Claims

1. A process for the elimination of mercaptans contained in gases by absorption in a hydrocarbon oil and regeneration of this oil, wherein the oil is regenerated by oxidation of the mercaptans that it contains, to form sulfonic acids, by carrying out this oxidation at the temperature and the pressure of absorption by means of an oxidant in an aqueous medium, the regenerated oil being recycled after separation of the aqueous phase containing the sulfonic acids in solution.

2. A process according to claim 1, wherein the oxidant is hydrogen peroxide.

3. A process according to claim 1, wherein the oxidant is a peracid.

90 4. A process according to claim 3, wherein the peracid is performic acid.

5. A process according to claim 3, wherein the peracid is formed in situ from the reaction of carboxylic acid and hydrogen peroxide.

95 6. A process according to claim 5, wherein the carboxylic acid/hydrogen peroxide molar ratio varies between 0.1/1 and 1/1.

7. A process according to claim 5, wherein 3 to 100 moles of hydrogen peroxide per mole of mercaptan are used.

8. A process according to any one of claims 5 to 7, wherein the aqueous effluents of the reaction are recycled after their titre adjustment by addition of hydrogen peroxide and carboxylic acid.

105 9. A process according to claim 1, wherein the temperature varies between 20 and 60°C.

10. A process according to claim 1, wherein the pressure varies between 5 and 10 MPa.

110 11. A process according to one of claims 1 to 10, wherein the oil is spindle oil, 100 NS oil, or any refinery cut having viscosity and vapor pressure between 20 and 60°C, almost equivalent to those of the above-mentioned oils.

12. A process for the removal of mercaptans contained in a gas comprising removing the mercaptans contained in the gas by absorption in a hydrocarbon oil, oxidising the mercaptans the oil contains to form sulfonic acids, said oxidation being carried out at the temperature and pressure of absorption by means of an oxidant in aqueous

-medium, and separating from the oil the aqueous phase containing the sulfonic acids in solution.

13. A process substantially as hereinbefore described with reference to the Example.

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